T H E S I S.

THE ACTION OF NITRIC ACID

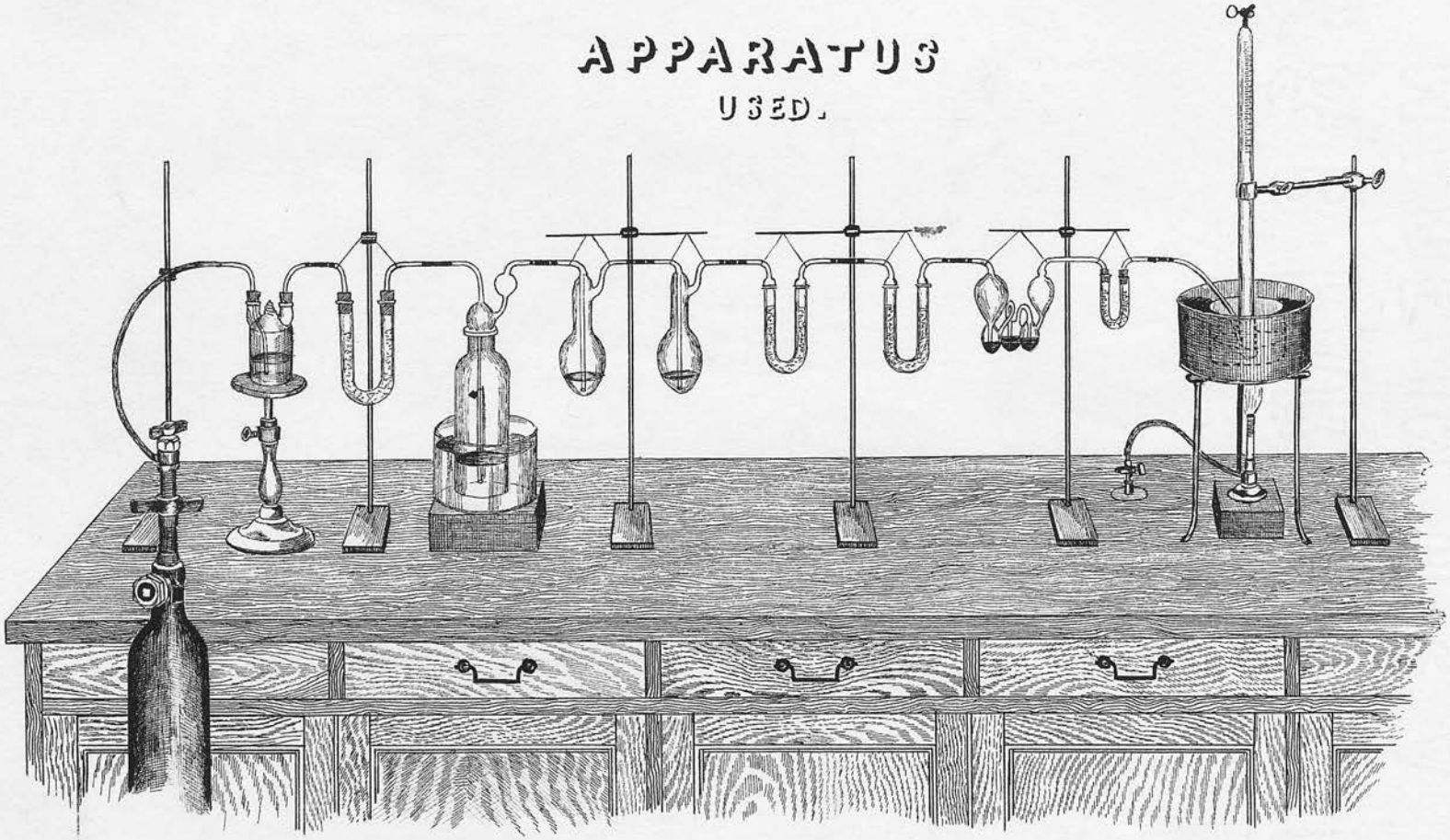
on

COPPER AND ZINC,

AND ON ALLOYS AND MIXTURES OF THESE METALS.

By SAMUEL WALKER, M.A., B.Sc., F.C.S.

APPARATUS USED.



THE ACTION OF NITRIC ACID ON COPPER AND ZINC, and on ALLOYS AND MIXTURES OF THESE METALS.

By SAMUEL WALKER, M.A., B.Sc., F.C.S.

The action of the different metals on nitric acid is a subject which has, despite the difficulties of the problem, exercised a great fascination over chemists, and has been the subject of laborious investigation by not a few. In 1870 St Claire Deville made a careful investigation of the ammonia produced by the action of dilute nitric acid on zinc.

Comptes rendus 70 pp. 20 & 550.

Acworth and Armstrong in 1876 carried out a long series of experiments on the action of nitric acid on copper, zinc and other metals, entirely confining their attention, however, to the nitric and nitrous oxides and the nitrogen produced in the reactions..

Chem. Soc. Jour. 1877 Vol. 2 p. 54.

In 1892 C. Montemartini published an account of a most exhaustive research he had made on the action of nitric acid of various strengths upon zinc, copper, silver, tin, iron, etc., in which he investigated all the products of the /

the reactions.

Gazetta Chimica Italiana 22.1. 1892.

and about the same time the first results of an investigation of a similar kind were published by Freer and Higley. Amer. Chem. Jour. 15.71. This investigation has since been continued.

Amer. Chem. Jour. 17.20; 18.589; 21.377.

Other Chemists have taken up their attention with special reactions and products, notably,

Russell Chem. Soc. Jour. 1874 p. 3.

Divers " " " 1883 p. 443.

and Veley Proc. Roy. Soc. Vol 46 p. 216.

With regard to alloys comparatively little has been done. Messrs Calvert and Johnson made an examination of the loss sustained by a given surface of alloy in a given time when exposed to dilute nitric acid. They found that what they call Zn_2 Cu or an alloy containing 67.26 per cent zinc and 32.74 per cent copper lost 54 times as much in a given time as Zn. Cu which contains 50.95 per cent Zinc and 49.05 per cent Copper, and generally that the action of the acid on alloys rich in zinc is comparatively violent, and that the action on those in which there is excess /

excess of copper is very much less.

Chem. Soc. Jour. 1866 19. 434.

Acworth and Armstrong too applied the method which they had used for the metals to two specimens of alloy, one of brass and the other of gun-metal . The brass they employed contained 30.2 per cent zinc, 69.1 per cent copper and .7 per cent of lead and tin, and they found with regard to this alloy that so far as the nitric and nitrous oxides and nitrogen are concerned, it behaved like pure copper.

Chem. Soc. Jour. 1877 p. 88.

I undertook this research more than two years ago at the suggestion of Professor Crum Brown, because experiments were being begun at that time for the purpose of determining the heat of formation of alloys, by observing the difference of rise of temperature in dissolving an alloy in nitric acid from that in dissolving a mixture of corresponding proportions, and it seemed desirable to the full solution of the problem that the nature and the proportion of the products obtained by dissolving in this acid both alloys and mixtures should be determined.

I hoped that the results obtained might contribute some material facts towards the elucidation of the nature of alloys /

alloys; whether so far as dissolution in acid is concerned an alloy behaves like a mixture of metals, or like a substance having a character peculiar to itself. I thought that some light might also be thrown on the reason of differences of the behaviour of the metals when dissolved in this way.*

A good deal of the time was spent by me in making preliminary experiments for the purpose of determining the best methods of collecting the products separately, and thus ascertaining the proportions, in which they are formed. I spent some time also in making and analysing the alloys. The results which I have obtained and tabulated in this paper were got from experiments carried out in the Chemical Laboratory of George Heriot's School, between April and September of this year.

I have confined my attention to the metals copper and zinc. These were chosen because both are acted on readily by nitric acid, and alloys of different proportions comparatively easily formed. Copper and Zinc the purest procurable /

x x x x x x x

* Results of these experiments by Dr Galt have since been published.

Phil. Mag. April 1900. See also
Baker Proc. Chem. Soc. Sept. 1899.

procurable, were obtained from Harrington Bros. of Cork and London, the zinc in rods, the copper in foil. At first I endeavoured to make the alloys in different proportions myself, using a Fletcher's Injector Furnace, but I found that though I was quite successful in making those with a large proportion of copper, I could not get the alloys, in which zinc predominates, homogeneous, owing to the small quantities with which I could work and the volatility of the zinc. I therefore got a set of alloys made by Harrington of pure copper and zinc, which accord very closely with what I requested them to make, and which are all very homogeneous. I asked for the set as follows :-

90 per cent Copper, 10 per cent zinc.

80 per cent Copper, 20 per cent zinc.

and so on down to 10 per cent copper and 90 per cent zinc. I have called them Nos. 1, 2, 3, 4, 5, 6, 7, 8 and 9. I have made a careful analysis of them all. using the electrolytic method for determining the copper, and estimating the zinc in the oxide, after precipitating as carbonate, and igniting.

The composition of the alloys obtained is :-

No. /

No. 1.	Copper	89.65	No. 2.	Copper	80.31
	Zinc	10.35		Zinc	19.66
No. 3.	Copper	69.98	No. 4.	Copper	60.88
	Zinc	29.79		Zinc	39.04
No. 5.	Copper	50.56	No. 6.	Copper	39.21
	Zinc	49.36		Zinc	60.75
No. 7.	Copper	29.48	No. 8.	Copper	16.76
	Zinc	70.38		Zinc	83.19

No. 9. Copper 11.89
Zinc 88.03

It will be observed, that all except Nos 8 and 9 agree fairly well with the proportions aimed at. The last two do not, however, but this is not surprising, when account is taken of the difficulty of producing them owing to the volatility of the zinc. Here I may remark, that I am at a great loss to understand, how it was possible for Messrs Calvert and Johnson to produce alloys exactly corresponding to the formulae Cu_5 Zn, Cu_4 Zn, etc., etc.

Chem. Soc. Jour. 1866 XIX. 434

It being necessary to the collection of the products in a pure state, that air be excluded from the apparatus, various methods have been employed of accomplishing this. Acworth /

Acworth and Armstrong exhausted their apparatus of air by means of a Sprengel pump. This method seemed to me one of great difficulty, not the smallest being that of keeping the apparatus air tight, as these chemists found in their experiments. Montemartini conducted the solution of the metal in the acid in a neutral atmosphere of carbonic acid, and Freer and Higley in their experiments made use of a similar device.

The method which I used is, with slight modification, that of Montemartini. The apparatus consists of a Drechsel bottle, in the upper part of which I fixed a little platinum shelf, on which the metal or alloy to be dissolved is placed. The acid is put into this bottle, and a short-range thermometer is suspended inside it so as to dip into the acid. The exit tube of the bottle is connected with two Cluez bulbs by india rubber tubing, which, especially when strong acid is used, is coated inside with paraffin wax. In these bulbs is put a saturated solution of bicarbonate of soda, which absorbs the nitrogen peroxide, passing in, forming sodium nitrate and nitrite.

$$2\ NO_2 + 2\ Na\ HCO_3 = Na\ NO_3 + Na\ NO_2 + H_2O + 2\ CO_2$$

The bulbs are connected with two U-tubes filled with calcium chloride, to thoroughly dry the gases passing through /

through, and these again are joined on to a set of Geissler bulbs containing a strong solution of chromic acid in 12 per cent. nitric acid, which absorbs the nitric oxide. (This is a method described by C. Böhmer Zeit. für Anal. Chem. XXI. 212 and XXII. 20.

I tried the absorbing power of the solution on nitric oxide, and found it absorbed the gas greedily, being instantaneously blackened on account of the reduction of the chromic acid the nitric oxide being oxidised to nitric acid). Connected with this, and weighed along with it, is a small U-tube of calcium chloride, to prevent loss of weight by escape of water vapour. A bent glass tube leads from this to a small pneumatic trough in which is a solution of caustic soda, one of soda to ten of water, which is kept at a temperature of 70°-80° C by being placed in a metal vessel of water, heated by a bunsen. The gases nitrous oxide and nitrogen, which have escaped absorption previously, are collected here in a long tube filled with the caustic soda. I tried the solubility of nitrous oxide in caustic soda, and found that it is slightly soluble in the cold, but in the heat unappreciably so. I did not saturate the soda with the gas, as had been suggested, because I thought it might rather produce error in the opposite /

opposite direction.

As has been already stated, carbonic acid is used to give a neutral atmosphere. It is supplied from a cylinder to the Drechsel bottle through a wash-bottle and drying tube. At first I used a Kipps apparatus, containing marble and hydrochloric acid, freed from air to produce the carbon dioxide; but I found that I did not get a uniform, and often not a great enough pressure, nor did I succeed in getting the gas completely free from air. By means of the cylinder I can get a very uniform current and constant pressure. The only objection is that the carbonic acid is not free, and apparently cannot be got entirely free, from air.* I made, however, a number of blank experiments allowing the gas to pass through the apparatus at a constant rate, and noting how much gas was collected per hour over the caustic soda. I found that at the rate I used in my experiments 1.2 c.c. was the average volume per hour. Allowance /

x x x x x x x

* The Manufacturers guarantee the cylinder to contain 99¾ per cent. CO_2.

Allowance was made for this in all the experiments. The experiments were carried through as follows :- the acid was measured out into the bottle, the weighed metal or alloy placed upon the shelf, and the apparatus joined up. In all the experiments with 42.5 per cent. acid (sp. gr. 1.266) the volume used was 75 c.c. The current of carbonic acid was then turned on and allowed to pass through the apparatus, till all the air was expelled, and till only tiny bubbles of air (the impurity in the carbonic acid) were rising through the hot soda. The Geissler bulbs containing the chromic acid, with calcium chloride tube attached, were then disconnected, little caps put on the ends, and weighed. The apparatus was then connected up again, and the current allowed to pass for a little to make sure that, if air had entered, it was again expelled. The Drechsel bottle was then slightly inclined, and a gentle shake given to it, when the metal dropped into the acid, and action began. The gaseous products are carried forward by the carbonic acid, which also serves by keeping the acid in constant motion, to prevent the accumulation of salt on the surface of the metal, and so cause it to present fresh surfaces to the acid /

acid, as well as, to a certain extent, to keep the temperature constant throughout the liquid. The temperaturs was noted at the beginning, and during the time that the metal was being dissolved. In all the experiments the acid was used in large excess of what was required to dissolve the metal, 10 to 15 times, and the temperature of it was kept as far as possible constant, by surrounding the bottle with cold water, and in some cases, owing to the violence of the reaction, with melting ice. The acid, which I used in most of the experiments, was strong, pure, nitric acid, diluted with its own volume of water. The specific gravity of this diluted acid was 1.266, and its percentage of nitric acid, determined by standard solution of sodium carbonate, was 42.5.

I chose this strength, because with a more dilute acid some of the alloys used took a very long time to dissolve, and on the other hand, with a stronger acid the action on others was rather violent. I have confined my attention to the final products, and have in every case sought for nitrogen peroxide, (including nitrous acid), nitric oxide, nitrous oxide, nitrogen and ammonia. I have also endeavoured

to /

to do what has been done by few experimenters in the same field before, viz., to determine all the products of a given reaction, and so account for all the metal used up.

The various products were determined by me as follows:- After the metal had all been dissolved, I allowed the carbonic acid to continue passing, till the gas collecting over the soda was in the same tiny bells as before, indicative of impurity in the carbonic acid only. The Geissler bulbs were first disconnected and weighed. The increase of weight gives the weight of the nitric oxide produced. The solution in the Drechsel bottle was then diluted with water to a certain given volume (200 c.c. usually), care being taken that any red gas in the bottle was dissolved also. Part of this solution was used to test for the nitrogen peroxide, by means of a standard solution of potassium permanganate. The remainder of it was employed to test for the ammonia, which was driven out by means of strong caustic soda, passed into a standard solution of sulphuric acid and titrated with a standard solution of potash.

The solution in the Cloez bulbs was washed out, made up /

up to a given volume, and tested for nitrous acid by means of permanganate. The gas collected over the soda was transferred to a gas burette over mercury, and measured. It was then, part at a time, mixed with hydrogen, and with a certain volume of oxygen and hydrogen (Knall gas), and exploded. The volume of nitrous oxide was thus determined. The nitrogen was estimated by difference. As has been already stated, allowance was made for the impurity: further, before mixing with hydrogen, the gas was transferred to a double gas-absorption pipette, containing alkaline pyrogallate so that, if any oxygen was present, it might be removed and further information gained as to the amount of impurity. In no case was the volume more than what might be called insignificant, and it usually corresponded very well with what might be expected from the total quantity of impurity. In order to further test the method, I made a quantitative determination of lead nitrate, using the apparatus exactly in the way described, except that a hard glass tube in which the lead nitrate was heated took the place of the Drechsel bottle. The oxygen was collected over the soda.

	Found	Calculated.
Lead oxide	67.17	67.27
Nitrogen peroxide	27.27	27.88
Oxygen	4.91	4.85
	99.35	100

I/

I made four determinations with the pure metals copper and zinc, and I give below the weights of the products obtained from 1 gramme of metal, with the calculated weight of metal used up in the formation of those products. It is immaterial for this, what theory is held with regard to the reduction of the nitric acid, whether by nascent hydrogen or by direct oxidation.

Copper.

	A		B		C		D	
		Metal		Metal		Metal		Metal
Nitrogen Peroxide	.7360	.5040	.9034	.6187	.8942	.6123	.9485	.6495
Nitric Oxide	.1159	.3651	.0816	.2570	.0735	.2315	.0825	.2598
Nitrous Oxide	.0050	.0286	.0043	.0246	.0036	.0206	.0030	.0172
Nitrogen	.0023	.0259	.0014	.0158	.0021	.0236	.0013	.0146
Ammonia	0	0	0		0		0	
Total Metal		.9236		.9161		.8880		.9411

It will be noticed that in every case the metal falls short of 100 per cent, but in these experiments, as in all, the nitrous acid and nitrite produced were calculated as if produced from nitrogen peroxide, whereas reduction may have gone further, and some nitrous acid may have thus been formed directly. /

directly. If this is what takes place a greater weight of metal would thus be accounted for and the deficiency explained.

It will also be noticed that nitrous oxide and nitrogen were obtained. I say this because Montemartini (loc. cit.) states that no nitrous oxide and nitrogen are produced by the action of nitric acid of any strength on copper. My experiments seem to lead to an opposite conclusion for I obtained in each case a small, but perfectly distinct volume of gas which could be analysed. Montemartini got some gas over the soda, but he attributed it to impurity in the carbonic acid (loc. cit. P. 397) and it amounted to only 1 c.c. in four hours. In each of the four experiments, I noticed that, while the action was going on, larger bubbles of gas passed up through the soda than the tiny ones seen, before the metal was dropped into the acid, and of course a greater volume of gas was collected than in the blank experiments. In the four experiments with acid of 42.5 per cent I got after making allowance for impurity 4.3, 3.3, 3.5, and 2.7 c.c. of gas at N. T. P.

The mixture was analysed and the result was as stated.

With acid of 56.7 per cent one experiment was done,

1/

1 gm. of metal dissolved in 60 c.c. acid gave 3 c.c. of gas. These results are more in accord with those of Acworth and Armstrong (loc. cit.) My results for the nitrogen peroxide and nitric oxide agree fairly well with those of Montemartini. Freer and Higley corroborate Montemartini with regard to the nitrous oxide and nitrogen, but they go further, and state that no nitric oxide is produced with nitric acid stronger than sp. gr. 1.25. Now the acid I used has sp. gr. 1.266, and I got nitric oxide What was its source ?

The average of the results of the four experiments gives for 1 gm. of metal :-

Nitrogen Peroxide .8705

Nitric oxide .0884

With acid the sp. gr. of which was 1.355 and the percentage of acid 56.7 the results were :-

Nitrogen Peroxide 1.2116

Nitric Oxide .0235

The nitric oxide could not have been produced by the action of the nitrogen peroxide on the water of the solution of carbonate of soda, for, with the greater quantity of nitrogen peroxide, there would have been a greater quantity of nitric oxide, but this is not the case. Therefore we must conclude that the nitric oxide was produced in the acid solution./

solution. It is produced there, I believe, by the action of the nitrogen peroxide on the water in the excess of the acid solution. It seems undoubtedly the case, that nitrogen peroxide is the predominating product (perhaps the only one with concentrated acid). Even with acid of 42.5 per cent, it will be noticed that the quantity of the nitrogen peroxide is practically ten times that of the nitric oxide ; with acid 56.7 per cent, it is more than 50 times.

I may say that I find my results for nitrogen peroxide and nitric oxide, so far as comparable, agree with those of Montemartind.

My experiments with zinc gave the following results, which are stated in the same way as those for copper :-

Zinc.

	A		B		C		D	
Nitrogen Peroxide	.2194	Metal .1550	.1973	Metal .1394	.1610	Metal .1138	.1725	Metal .1219
Nitric Oxide	.0066	.0215	.0071	.0237	.0051	.0166	.0079	.0257
Nitrous Oxide	.0201	.1241	.0355	.2098	.0394	.2328	.0414	.2446
Nitrogen	.0056	.0650	.0059	.0685	.0073	.0847	.0072	.0836
Ammonia	.0366	.5597	.0392	.5995	.0385	.5888	.0374	.5720
		.9253		1.0409		1.0367		1.0478

The /

The results of A do not agree very well with B, C, and D, especially as regards the Nitrous oxide, but temperature seems to affect the production of this gas, to a great extent. In A the temperature of the acid rose to 30° C. a higher temperature than was reached in any of the others. Whether this is the explanation of the matter or not, I am not certain, but I may say that with the alloys as well, a higher temperature noticeably gave a less volume of this gas. The maximum quantity is in D, but this is only half of what Montemartini gives as his result for about the same concentration of acid. This is somewhat perplexing, and it is rendered still more so by his stating that his results require 1.2285 gm of metal for their production whereas only 1 gm was used. I give below his results compared with the average results of my four experiments.

	Montemartini.		My average result.	
		Metal		Metal
Nitrogen Peroxide	.1800	.1250	.1875	.1284
Nitric Oxide	.0060	.0195	.0067	.0218
Nitrous Oxide	.0828	.4892	.0341	.2015
Nitrogen	.0050	.0580	.0065	.0825
Ammonia	.0351	.5368	.0379	.5796
Total Metal		1.2285		1.0138

Montemartini /

Montemartini (Gazetta 22.1. 342) makes the anomalous weight of metal calculated, the basis for his argument, that water intervenes in the reaction between zinc and nitric acid, a statement, which in the sense in which it must be understood, if it is to be of any real value in explaining the anomaly, is not borne out by facts. It is to be noted in this connection that Montemartini did not determine all the products of the dissolution of a given piece of zinc, but determined the ammonia by dissolving one piece, and the other products by dissolving another. Probably he would have found, that, in the conditions of the experiment in which he obtained so much nitrous oxide, a much smaller quantity of ammonia was produced. I believe that the relative amounts of nitrogen peroxide and nitric oxide on the one hand, and of nitrous oxide and ammonia on the other are so dependent on the conditions of the experiment, that there is no sure way of ascertaining the total amount of metal used in producing the different gases but that of determining all the products of a single reaction. The results of B, C and D give over 100 per cent. of metal but this is probably due to errors of experiment, a little difference in the ammonia, for example, giving a great difference /

difference in the metal. I am inclined to believe that my results for ammonia are rather overstated, as in two other experiments, which I did with zinc, while the other products agree very well with those given, the average result for ammonia comes out .0346.

I give the average result of the four experiments with copper and zinc.

	Copper.	Metal.	Zinc.	Metal.
Nitrogen Peroxide	.8705	.5961	.1875	.1284
Nitric Oxide	.0884	.2785	.0067	.0218
Nitrous Oxide	.0040	.0229	.0341	.2015
Nitrogen	.0018	.0203	.0065	.0825
Ammonia	0	0	.0379	.5796
Total Metal		.9178	Total Metal	1.0138

ALLOYS /

A L L O Y S .

With each of the alloys two experiments were made. The weights of the products, as well as the calculated weight of metal dissolved in producing them, are given. The temperature of the acid solution during the reaction is also given. I did not attempt to keep the temperature of the acid constant; indeed the experiment was usually carried out at the ordinary temperature of the air, but in some cases, where the action was pretty violent, I cooled the acid before the metal was dropped into it by means of melting ice. For convenience the experiments are arranged in two sets A and B. In A the temperature is generally lower than in B.

No. 1. Alloy.

	A		B	
	Temp. 12°-14°	Metal	Temp. 15°-16°	Metal
Nitrogen Peroxide	.6813	.4680	.7976	.5478
Nitric Oxide	.1013	.3201	.0903	.2853
Nitrous Oxide	.0169	.0971	.0108	.0621
Nitrogen	.0052	.0587	.0031	.0349
Ammonia	0	0	0	0
Total weight of metal		.9439		.9301

No. /

No. 2. Alloy.

	A. Temp. 12°-14°	Metal	B. Temp. 15°-16°	Metal
Nitrogen Peroxide	.6786	.4677	.7829	.5397
Nitric Oxide	.0973	.3078	.0842	.2669
Nitrous Oxide	.0179	.1032	.0144	.0830
Nitrogen	.0038	.0430	.0046	.0521
Ammonia	0	0	0	0
Total Metal		.9217	Total Metal	.9417

No. 3. Alloy.

	A. Temp. 12°-14°	Metal	B. Temp. 15°-17°	Metal
Nitrogen Peroxide	.6569	.4541	.7148	.4943
Nitric Oxide	.0860	.2735	.1086	.3453
Nitrous Oxide	.0177	.1125	.0092	.0585
Nitrogen	.0015	.0170	.0034	.0390
Ammonia	0	0	0	0
Total Metal		.8571	Total Metal	.9371

No. /

No. 4. Alloy.

	A. Temp. 13°-15°	Metal	B. Temp. 15°-17°	Metal
Nitrogen Peroxide	.6606	.4581	.7539	.5228
Nitric Oxide	.0829	.2645	.0952	.3037
Nitrous Oxide	.0304	.1763	.0155	.0899
Nitrogen	.0055	.0627	.0023	.0272
Ammonia	0	0	0	0
	Total Metal	.9616	Total Metal	.9436

No. 5. Alloy.

	A. Temp. 13°-15°	Metal	B. Temp. 15°-17°	Metal
Nitrogen Peroxide	.5489	.3818	.6284	.4371
Nitric Oxide	.0796	.2547	.0805	.2576
Nitrous Oxide	.0323	.1903	.0242	.1408
Nitrogen	.0061	.0706	.0075	.0857
Ammonia	0	0	0	0
	Total Metal	.8974	Total Metal	.9212

No. 6. Alloy.

	A. Temp. 14°-15°	Metal	B. Temp. 16.5°-19°	Metal
Nitrogen Peroxide	.4853	.3383	.6302	.4398
Nitric Oxide	.0500	.1605	.0474	.1522
Nitrous Oxide	.0597	.3484	.0386	.2253
Nitrogen	.0061	.0699	.0075	.0859
Ammonia	0	0	0	0
	Total Metal	.9171	Total Metal	.9032

No. /

No. 7 Alloy.

	A		B	
	Temp.5°-9°	Metal	Temp.7°-12°	Metal
Nitrogen Peroxide	.2001	.1401	.2406	.1684
Nitric Oxide	.0160	.0516	.0080	.0258
Nitrous Oxide	.0867	.5075	.0757	.4432
Nitrogen	.0088	.1012	.0075	.0863
Ammonia	.0126	.1927	.0125	.1912
	Total Metal	.9931	Total Metal	.9149

No. 8 Alloy.

	A		B	
	Temp.6.5°-12	Metal	Temp.17°-24°	Metal
Nitrogen Peroxide	.2176	.1528	.2148	.1518
Nitric Oxide	.0104	.0336	.0211	.0686
Nitrous Oxide	.0818	.4804	.0716	.4231
Nitrogen	.0079	.0911	.0072	.0836
Ammonia	.0168	.2553	.0145	.2210
	Total Metal	1.0132	Total Metal	.9481

No. 9 Alloy.

	A		B	
	Temp.5°-12°	Metal	Temp.13°-20°	Metal
Nitrogen Peroxide	.2233	.1573	.2020	.1423
Nitric Oxide	.0086	.0279	.0748	.0481
Nitrous Oxide	.0767	.4519	.0700	.4124
Nitrogen	.0064	.0741	.0058	.0671
Ammonia	.0198	.3019	.0212	.3242
	Total Metal	1.0131	Total Metal	.9941

Determinations of the products of the action of the same strength of acid upon mixtures of the metals in all the proportions were made, and the results are given in the tables which follow.

In the first column is given the weights of the products, which would be obtained from the corresponding weights of copper and zinc, if they were dissolved separately. In the second column are given the weights of the products actually found, and in the third the calculated weights of metal dissolved in the formation of these products.

MIXTURES

No. 1.
0.9 Copper 0.1 Zinc.

	Calculated	Found	Metal
Nitrogen Peroxide	.8023	.7981	.5466
Nitric Oxide	.0803	.0840	.2646
Nitrous Oxide	.0070	.0048	.0275
Nitrogen	.0023	.0018	.0202
Ammonia	.0038	.0058	.0851
		Total Metal	.9440.

No/

MIXTURES

No. 2.
0.8 Copper 0.2 Zinc.

	Calculated	Found	Metal
Nitrogen Peroxide	.7339	.6836	.4681
Nitric Oxide	.0720	.0838	.2640
Nitrous Oxide	.0100	.0063	.0361
Nitrogen	.0027	.0021	.0236
Ammonia	.0076	.0113	.1729
		Total Metal	.9647

No. 3.
0.7 Copper 0.3 Zinc.

Nitrogen Peroxide	.6657	.6615	.4602
Nitric Oxide	.0639	.0748	.2394
Nitrous Oxide	.0130	.0061	.0355
Nitrogen	.0033	.0023	.0263
Ammonia	.0113	.0123	.1874
		Total Metal	.9488

No. 4.
0.6 Copper 0.4 Zinc.

	Calculated	Found	Metal
Nitrogen Peroxide	.5973	.6182	.4298
Nitric Oxide	.0557	.0470	.1500
Nitrous Oxide	.0160	.0089	.0518
Nitrogen	.0037	.0040	.0457
Ammonia	.0152	.0192	.2891
		Total Metal	.9664

MIXTURES

No.5
C.5 Copper 0.5 Zinc.

	Calculated	Found	Metal
Nitrogen Peroxide	.5291	.5129	.3568
Nitric Oxide	.0476	.0639	.2045
Nitrous Oxide	.0191	.0089	.0518
Nitrogen	.0042	.0045	.0514
Ammonia	.0190	.0224	.3379
		Total Metal	1.0024

No. 6
0.4 Copper 0.6 Zinc.

Nitrogen Peroxide	.4607	.4536	.3236
Nitric Oxide	.0394	.0480	.1536
Nitrous Oxide	.0221	.0108	.0628
Nitrogen	.0046	.0043	.0491
Ammonia	.0227	.0255	.3840
		Total Metal	.9731

No. 7
0.3 Copper 0.7 Zinc.

Nitrogen Peroxide	.3925	.3685	.2564
Nitric Oxide	.0312	.0373	.1194
Nitrous Oxide	.0251	.0106	.0998
Nitrogen	.0051	.0055	.0629
Ammonia	.0265	.0306	.4608
		Total Metal	.9993

No./

MIXTURES

No. 8
0.2 Copper 0.8 Zinc.

	Calculated	Found	Metal
Nitrogen Peroxide	.3241	.3358	.2373
Nitric Oxide	.0231	.0146	.0475
Nitrous Oxide	.0281	.0109	.0638
Nitrogen	.0055	.0039	.0453
Ammonia	.0302	.0357	.5460
		Total Metal	.9399

No. 9
0.1 Copper 0.9 Zinc.

Nitrogen Peroxide	.2559	.1868	.1298
Nitric Oxide	.0148	.0044	.0143
Nitrous Oxide	.0311	.0286	.1690
Nitrogen	.0061	.0099	.1149
Ammonia	.0341	.0374	.5720
		Total Metal	1.0000

Besides the tables I give diagrams of curves giving the same results in graphic form. In the case of the alloys the mean of the results of the two sets of experiments A and B is taken. In these the abscissae represent the percentage of zinc, while the ordinates represent the weights of the products obtained by dissolving 1 gm. of the alloy/

alloy or mixture. In diagrams I. and IV. the ordinates shew centigrams of product or metal, but in II. and III. they give the result in milligrams. This is done for the sake of comparing with one another the nitric oxide on the one hand and on the other the nitrous oxide and nitrogen, and the ammonia, apart from the nitrogen peroxide the amount of which in comparison with the others being so overwhelmingly great. In diagram I. I have put the nitrogen peroxide and nitric oxide together; I think I am justified in doing so, as I found in many experiments that an increase in the production of the one caused a diminution in the other and vice versa : neither have I represented the nitrogen by a separate curve, but have taken it along with the nitrous oxide. Diagram I. gives the nitrogen peroxide and nitric oxide for alloys and mixtures, the curve of the alloys being in red ink. An examination of it shews that, while the amount of these gases derived from a mixture of the metals does not vary much from the straight line joining copper and zinc and representing, what should be got from the metals if dissolved separately, the amount from the alloys shows a very considerable deviation from this. There is at once a remarkable falling off in the amount of product greater than in the case of the mixture. Then the /

Then the amount remains almost constant till 4 is reached. Here there is a rapid fall to 5 and 6 and then a very rapid fall to 7, after which the amount remains almost constant and very little more than what is obtained from pure zinc. With regard to the mixtures, 9 shews the greatest variation from the normal. This mixture gave an abnormal result in other respects. Reference will be made to it again.

By diagram II. which gives in one set of curves the amount of the nitric oxide from alloys and mixtures, and in the other that of the nitrous oxide and nitrogen, some very striking and important facts are disclosed. The amount of nitric oxide from alloys 1, 2, 3 and 4, is pretty constant, the mean being greater than that derived from pure copper. 5 shews a considerably less amount, then there is a rapid fall to 6 and another to 7, when the weight of product remains practically constant and very little more than what is got from zinc itself.

In the case of the mixtures the amount of nitric oxide shews considerable variation from what might be expected, being generally much higher. In 4, 8, and 9, it is lower : in 4 and 8, however, it is to be noted that the nitrogen peroxide /

peroxide is greater than the normal amount, and if this increase be added on (on the same scale) to the weight of the nitric oxide got, it will be found that the curve, - represented at this part by a dotted line - corresponds well with the rest. In the case of 9 great abnormality is again shown.

With regard to the other curves, the one representing the alloys shows that from those rich in copper, a greater amount of nitrous oxide and nitrogen is obtained than from pure copper.

In 3 the amount slightly falls off but it is greater in 4 and in 5, after which it rapidly increases to 6 and then to 7, when it seems to reach a maximum, falling off in quantity in 8 and 9 and then enormously to pure zinc. This I cannot explain, but my experiments have all shewn that a far greater quantity of nitrous oxide was got from the alloys rich in zinc than from pure zinc. It must be borne in mind, however, that the quantity of ammonia derived from the pure zinc is very much greater than that from the alloys. In the case of the mixtures, the curve shews that the amount of the nitrous oxide and nitrogen obtained is very much less than the calculated amount. The fact that the /

the amounts of nitric oxide are higher, and those of nitrous oxide lower is, I think, capable of explanation. I noticed in all the experiments that, as soon as a little of the copper had dissolved in the acid, the zinc appeared to dissolve less rapidly, and behaved, and even looked like, copper. The zinc was evidently not dissolving directly in the acid, but was replacing copper, which was then dissolving. After a little then, nitrous oxide was scarcely produced at all, but only nitric oxide. This was not the case with 9, which contains the smallest quantity of copper. The amount of nitrogen peroxide and nitric oxide, is, as has been stated, less than the normal, and the amount of the nitrous oxide is greater; why this is so, I am not at all certain, but, at any rate, the results got show that this mixture acts almost the same as pure zinc. Diagram III. gives curves representing the weight of the ammonia produced. With the mixture of metals the amount of ammonia is in every case, greater, though not very much greater, than what we should get from the weight of the zinc used, if it were present alone. Arguing in the same way as was done with regard to the nitrous oxide, we should expect to get less ammonia instead of more by the replacement of the copper by zinc, because in that case we should /

should have copper instead of zinc, and copper gives no ammonia, but whatever is the cause it seems evident, at any rate, that the usual production of nitrous oxide is hindered by the presence of the copper, and that in its place there is an increased quantity of nitric oxide and of ammonia. With the alloys no ammonia is got till 7 is reached, and there the quantity is considerable. Where the origin of the curve is, I do not know, but it must be between 6 and 7. The amount increases in 8 and 9, and then to almost double in pure zinc.

It seemed to me, on looking into the problem of the production of these various substances, that a better idea might be got of the energy of the reactions, which produce them, by considering, not the weights of the products themselves, but that of the metal used up in their production. Therefore I have in diagram IV. given in one curve, the sums of the calculated weights of metal dissolved in producing the nitrogen peroxide and nitric oxide, and in another the sums of the weights required for the nitrous oxide, nitrogen and ammonia.* This has been done both for alloys and mixtures, the curves for the alloys being in red ink. The two /

x x x x x x x

* The number considered as the atomic weight was taken between 63 and 65 proportional to the weight of copper and zinc in the alloy or mixture.

two curves for the alloys and the two for the mixtures are of course complementary. The sums of the corresponding ordinates give the total weight of metal accounted for in each experiment.

An examination of the tables and the curves shows that, while a mixture of metals behaves on the whole like a mixture, an alloy behaves quite differently. The alloys rich in copper for example behave pretty much like pure copper and down to 4 which contains nearly 40 per cent zinc these alloys give practically the same products. About this point, however, a change takes place the zinc begins to assert itself, and there is a rapid falling off in the production of the nitrogen peroxide and nitric oxide, and an increase in the production of nitrous oxide and nitrogen. 5 and 6 are intermediate in their action. After this the character of the zinc seems to prevail, and so influences the copper alloyed with it, that the alloy acts as if it were zinc. This is particularly the case as far as the higher oxidation products, the nitrogen peroxide amd the nitric oxide, are concerned, but with regard to the other products, the nitrous oxide and ammonia, alloying with the copper seems to cause the ammonium nitrate /

nitrate which, no doubt, is first produced, to decompose and give a very much greater amount of nitrous oxide than is got from pure zinc. What these experiments have shewn, with regard to all the products of the various alloys, was noticed before by Acworth and Armstrong(Chem. Soc. Jour. 1877 p. 88) with regard to the production of nitric oxide, nitrous oxide and nitrogen, by dissolving a specimen of brass, nearly approaching in composition the one called 3, in nitric acid (1 of acid to 2 of water.) The behaviour of the alloys 7. 8. and 9 with regard to the products of dissolution in acid confirms, I think, what was observed by Laurie (Chem. Soc. Jour. Trans. 1888. p. 104) who found that, when the percentage of zinc in an alloy was more than 67, the alloy behaved in the Cuprous Iodide cell like zinc, shewing an electromotive force practically equal to that of the pure metal. The differences in the products, got by dissolving copper and zinc in nitric acid, are sufficiently striking to call for an explanation, and I beg respectfully to submit the following :- The great difference is due to the fact, that copper acts mainly, if not entirely, on the acid, by combining directly with the oxygen, while zinc acts by first replacing the hydrogen. Freer and Higley found /

found in their experiments on silver, copper, and iron, that the only product of the action of strong nitric acid on these metals is nitrogen peroxide , and Montemartini got a similar result. With strong acid, I found that the other products of the action on copper were exceedingly small, when compared with the nitrogen peroxide. Freer and Higley believe that the strong nitric acid acts on the metals by direct oxidation. This, I think too, is the natural inference from Veley's experiments on the action of dilute acid on copper. Veley, Armstrong, and others agree in stating that nitrous acid is the first product of the action of copper on nitric acid, and Veley proves (loc. cit.) that dilute nitric acid, free from nitrous acid, does not act on pure copper, nitrous acid having first to be formed. Now, if the action were one by nascent hydrogen, one would suppose that the reduction of the nitric acid would take place very readily even with dilute acid, some nitrous acid would thus be formed, and the action proceed very quickly. If again the action be one of direct oxidation, one would very naturally suppose that such an action would not take place quite so readily. This, I think then, is the case. In the case of zinc, on the other hand /

hand, I believe that the action is entirely different. Ammonia is always produced even with strong acid, as has also been shown by Montemartini. Further, my own experiments show, that more than half of the metal, dissolved in the 42.5 per cent acid, goes to the formation of ammonia. Another point to be noted is, that zinc is one of the metals which gives hydroxylamine with nitric acid, as is stated by Divers (loc. cit). The production of ammonia, of hydroxylamine and of nitrous oxide, the last, no doubt as a secondary product, tends to show, that the action of zinc on nitric acid is quite different from that of copper and is, as is usually believed, due in the first place to the replacement by the zinc of the hydrogen of the acid. Montemartini discards both theories, and thinks that a new theory is required to explain the action. The reason for his thinking this necessary has already been referred to. With regard to the production of nitrous oxide and nitrogen from copper, it has been shown that these are produced, when the metal is in excess, and that their production is due to the action of the copper nitrate, but what is the explanation of their production, when the acid is in excess, as in my experiments ? I am not certain, but would suggest that it is due to impurity in the copper. The copper which I used was as pure as

I. c/

I could get it, but was not absolutely so, containing .123 per cent. of impurity, chiefly iron. The presence of even a small quantity of impurity, in the form of another metal, exercises a great influence on the solution of a metal in acid, and may sometimes cause a great change in the products. Take for example the fact that the alloys rich in copper give more, though not a great deal more, nitrous oxide than the copper, or compare the nitrous oxide and ammonia got from zinc and from alloy 9. (Can this be the reason of Montemartini getting such a large quantity of nitrous oxide in the experiment which has already been referred to?) If these views are true, the explanation of the formation of the oxides of nitrogen by the action of copper or nitric acid, usually given in the text books, and commonly taught, must be given up. The actions will more properly be expressed thus :-

$$Cu + HNO_3 = CuO + HNO_2 \quad (a)$$

$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O \quad (b)$$

$$HNO_2 + HNO_3 = 2NO_2 + H_2O \quad (c)$$

Equation (c) represents an action which is reversible $2NO_2 + H_2O = HNO_3 + HNO_2$ (d), but it is well known that with excess /

excess of water the action is :- $3NO_2 + H_2O = 2HNO_3 + NO$ (e), and these probably represent all the products of pure copper on nitric acid. Equation (e) also represents a reversible action, as I found in the course of experimenting on the solubility of nitrous and nitric oxides in nitric acid. In passing pure nitric oxide into nitric acid, I noticed red gas was produced, and on standing a blue liquid. This is, of course, a matter of common knowledge, but it led me to see that all these substances so act on one another, that the conditions of the experiment play a very important part in determining the final products. It is for this reason that I have in my results considered the nitrogen peroxide and nitric oxide together. With regard to zinc, it is possible that direct oxidation may take place, for the nitrogen peroxide is still the predominant product, but the probability is that the production of the oxides of nitrogen and the ammonia is due to nascent hydrogen.

My attention having been drawn to Galt's work already referred to, I made a series of experiments, for the purpose of ascertaining, if the more concentrated acid, which he used, gave similar results. I did not overtake the complete set, but /

but did one experiment each with copper, zinc, and alloys and mixtures, 3, 5 and 7. I also did mixture 9, but through an accident I did not get a complete analysis. The Sp. gr. of the acid used is 1.355 and the percentage of nitric acid in it is 56.7.

The results are as follows :-

Copper.

		Metal.
Nitrogen Peroxide	1.2116	.8297
Nitric Oxide	.0235	.0740
Nitrous Oxide	.0049	.0281
Nitrogen	.0010	.0114
Ammonia	0	0
Total Metal		.9432

No. 3.

	Alloy.	Metal	Mixture.	Metal
Nitrogen Peroxide	1.2144	.8395	.9274	.6350
Nitric Oxide	.0176	.0570	.0215	.0677
Nitrous Oxide	.0073	.0422	.0118	.0676
Nitrogen	.0026	.0295	.0059	.0664
Ammonia	0	0	.0102	.1560
Total Metal		.9682	Total Metal	.9927

No. /

No. 5.

	Alloy.		Mixture.	
		Metal		Metal
Nitrogen Peroxide	1.0295	.7162	.6780	.4717
Nitric Oxide	.0127	.0406	.0292	.0934
Nitrous Oxide	.0268	.1559	.0103	.0599
Nitrogen	.0041	.0469	.0047	.0537
Ammonia	0	0	.0193	.2906
Total Metal		.9596	Total Metal	.9691

No. 7.

	Alloy.		Mixture	
		Metal		Metal
Nitrogen Peroxide	.5704	.3968	.6617	.4632
Nitric Oxide	.0049	.0159	.0175	.0563
Nitrous Oxide	.0637	.3706	.0121	.0708
Nitrogen	.0064	.0731	.0052	.0410
Ammonia	.0068	.1024	.0268	.4061
Total Metal		.9586	Total Metal	1.0374

Zinc.

		Metal
Nitrogen Peroxide	.5170	.3541
Nitric Oxide	.0060	.0195
Nitrous Oxide	.0281	.1660
Nitrogen	.0060	.0696
Ammonia	.0245	.3747
Total Metal		.9839

It /

It will be seen on examining these figures and the curves in Diagram V., representing the weight of metal used up in their production, the nitrogen peroxide and nitric oxide being given by one set of curves the rest of the products by another, that, speaking generally, the same state of matters holds as with the more dilute acid, only here there is a good deal more irregularity. Alloy 3 behaves like copper, giving for example an almost identical quantity of nitrogen peroxide, 5 is intermediate as with the other acid, and there is a great change to 7 which gives results approaching those from zinc.

The mixtures on the other hand, give results, which are very different and approximate more to what the metals would give if dissolved separately. The peculiar results, got in the case of mixtures with the weaker acid, are again visible here. The nitric oxide and ammonia are higher than what might be expected, while the nitrous oxide is always lower. The same retardation of the dissolving of the zinc, when copper was present, was again very noticeable, 1 gm. of zinc by itself dissolved in $2\frac{1}{2}$ minutes, while in the case of mixture 7, as soon as a little copper had dissolved, the action /

action slowed down, the zinc looked red, like copper, and it took 55 minutes to dissolve, although the conditions of temperature at the beginning were almost identical.

A fortnight ago Dr Galt call my attention to a series of experiments by Dr J. H. Gladstone (Phil. Mag. Aug. 1900) which I was not in the least aware of till then. Dr Gladstone has determined only two substances, the nitrous acid in the solution and the ammonia. His results for ammonia are the only ones, that can possibly be compared numerically with mine, but even with respect to these, there is some difficulty, as we did not use the same alloys and mixtures. There is general agreement however, and in several important points I am gratified at being in accord with that eminent chemist. He finds ammonia with mixtures in three different proportions, in each case greater than the theoretical amount. He finds ammonia with one alloy Cu 20.5 and Zn. 79.5 per cent and only a trace with any, that he tried, of a lower percentage of zinc, or with copper itself. My results with both concentrations of acid agree with these.

Dr Gladstone also argues that more nitric oxide must be got from the alloys than from copper : My experiments show /

show that, with the alloys rich in copper, this is indeed the case.

My grateful thanks are due to Dr Lowe, and through him, to the Governors of Heriot's School, for the opportunity given me of carrying out this work in the school laboratory. I am also much indebted to Mr John Scott, a former pupil, for the sketch of the apparatus used, which he has kindly made for me.

George Heriot's School,

20th November, 1900.

DIAGRAM I.

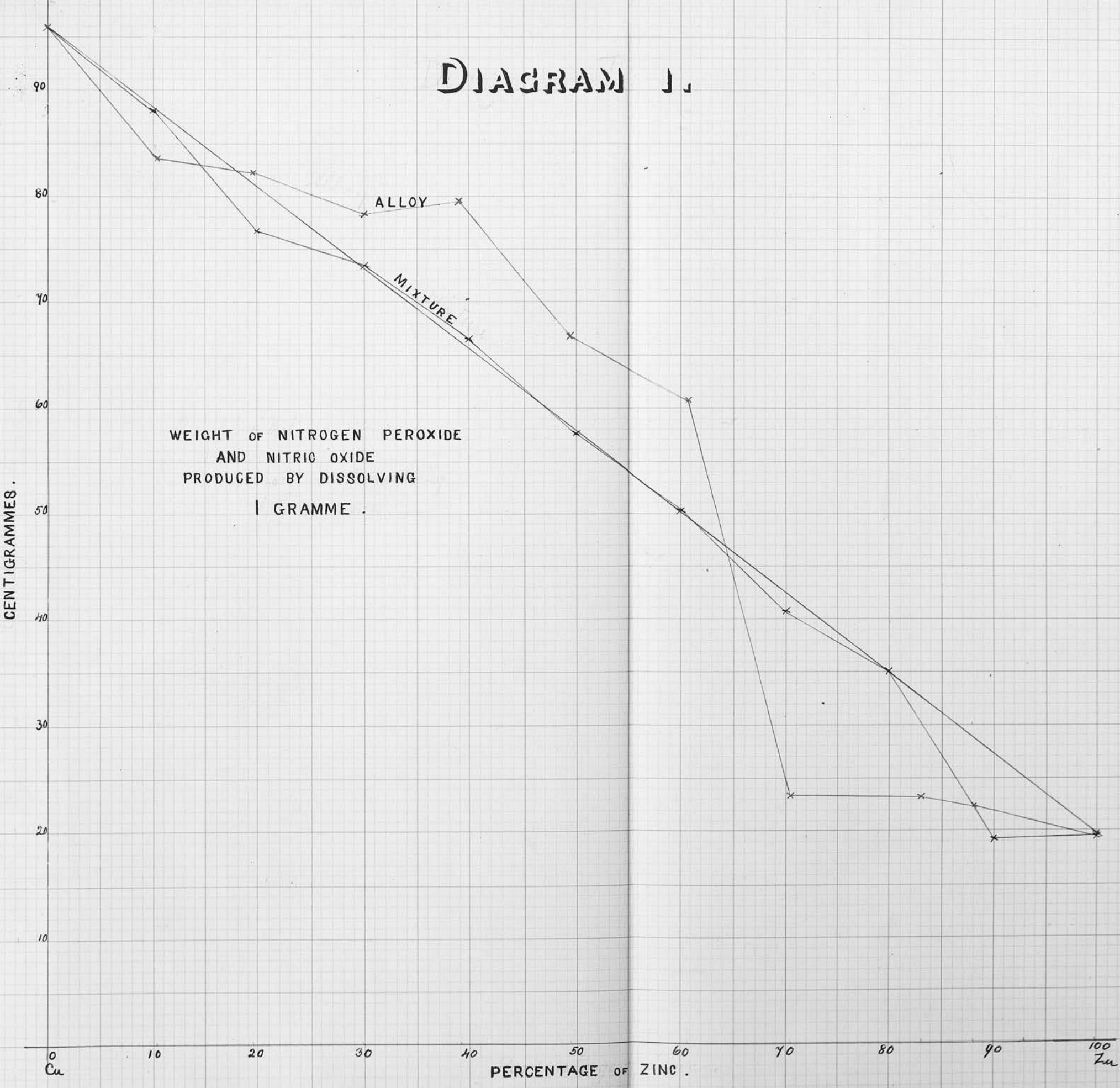

ALLOY
MIXTURE
WEIGHT OF NITROGEN PEROXIDE
AND NITRIC OXIDE
PRODUCED BY DISSOLVING
1 GRAMME .
CENTIGRAMMES.
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
Cu
Zn
PERCENTAGE OF ZINC .

DIAGRAM II.

WEIGHT OF NITRIC OXIDE AND
OF NITROUS OXIDE AND NITROGEN
PRODUCED BY DISSOLVING
1 GRAMME.

MILLIGRAMMES.

ALLOY NO

MIXTURE NO

ALLOY (N_2O+N_2)

MIXTURE (N_2O+N_2)

NO

NO

N_2O+N_2

(N_2O+N_2)

0 10 20 30 40 50 60 70 80 90 100

Cu

PERCENTAGE OF ZINC.

Zn

DIAGRAM III.

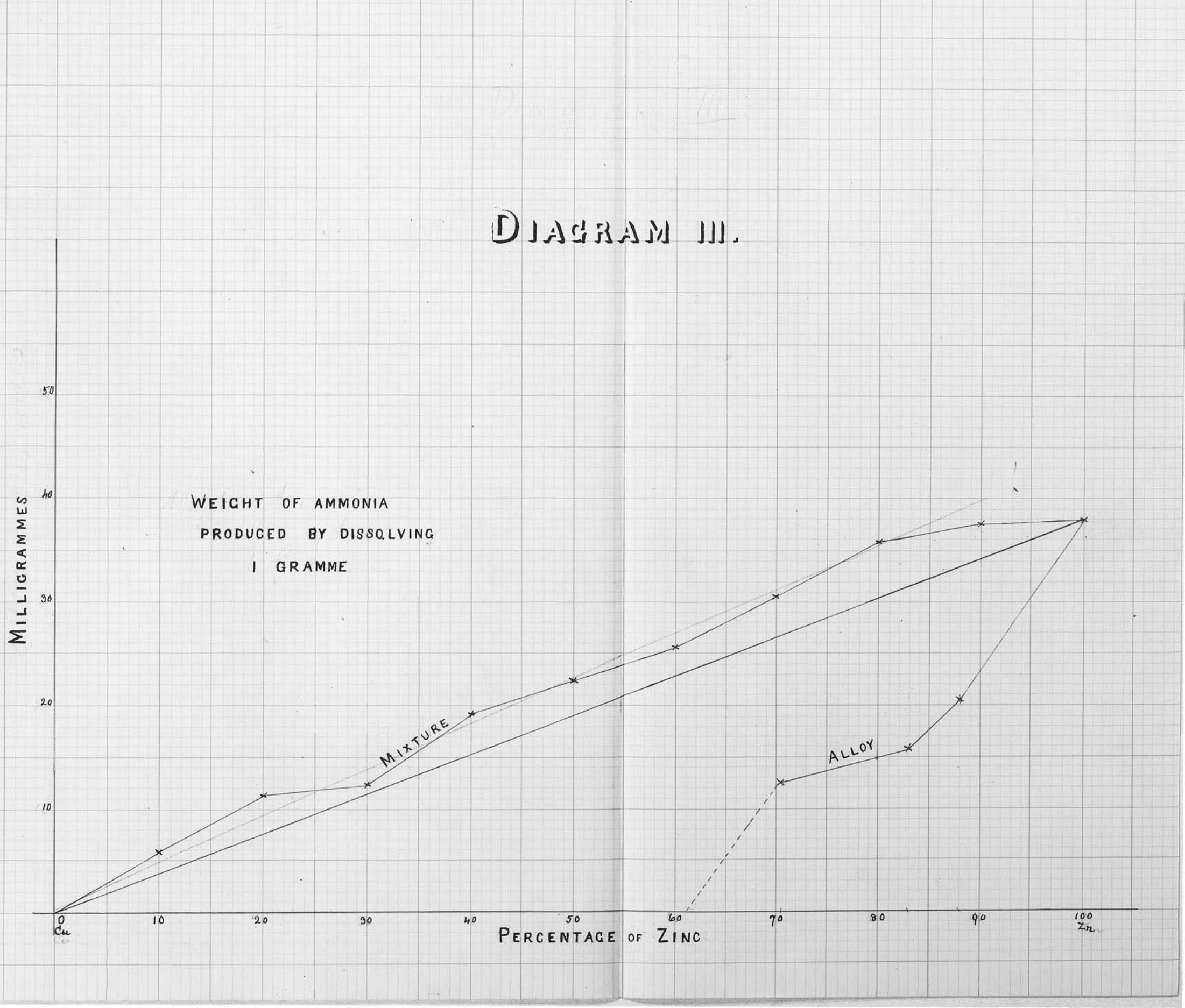

WEIGHT OF AMMONIA
PRODUCED BY DISSOLVING
1 GRAMME
MILLIGRAMMES
10
30
20
10
MIXTURE
ALLOY
0
Cu
10
20
30
40
50
60
70
80
90
100
Zn
PERCENTAGE OF ZINC

DIAGRAM IV.

ALLOY ($NO_2 + NO$)

MIXTURE ($NO_2 + NO$)

MIXTURE ($N_2O + N_2 + NH_3$)

ALLOY ($N_2O + N_2 + NH_3$)

Calculated WEIGHT OF METAL DISSOLVED

IN THE FORMATION OF

THE PRODUCTS

ACID 42·5 PER CENT

CENTIGRAMMES

90
80
70
60
50
40
30
20
10

0 Cu 10 20 30 40 50 60 70 80 90 100 Zn

PERCENTAGE OF ZINC

DIAGRAM V.

ALLOY. (NO_2+NO)

MIXTURE (NO_2+NO)

Calculated WEIGHT OF METAL DISSOLVED IN THE FORMATION OF THE PRODUCTS

ACID 56·7 PER CENT.

MIXTURE. ($N_2O+N_2+NH_3$)

ALLOY. ($N_2O+N_2+NH_3$)

CENTIGRAMMES

90 80 70 60 50 40 30 20 10

0 10 20 30 40 50 60 70 80 90 100

Cu

PERCENTAGE OF ZINC

Zn